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A physical model for the longitudinal polarizabilities of polymer chains

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The aim of this work is to provide a physical model to relate the polarizability per unit cell of oligomers to that of their corresponding infinite polymer chains. For this we propose an extrapolation method for the polarizability per unit cell of oligomers by fitting them to a physical model describing the dielectric properties of polymer chains. This physical model is based on the concept of a dielectric needle in which we assume a polymer chain to be well described by a cylindrically shaped nonconducting rod with a radius much smaller than its length. With this model we study in which way the polarizability per unit cell approaches the limit of the infinite chain. We show that within this model the macroscopic contribution of the induced electric field to the macroscopic electric field vanishes in the limit of an infinite polymer chain, i.e., there is no macroscopic screening. The macroscopic electric field becomes equal to the external electric field in this limit. We show that this identification leads to a relation between the polarizability per unit cell and the electric susceptibility of the infinite polymer chain. We test our dielectric needle model on the polarizability per unit cell of oligomers of the hydrogen chain and polyacetylene obtained earlier using time-dependent current-density-functional theory in the adiabatic local-density approximation and with the Vignale-Kohn functional. We also perform calculations using the same theory on truly infinite polymer chains by employing periodic boundary conditions. We show that by extrapolating the oligomer results according to our dielectric needle model we get good agreement with our results from calculations on the corresponding infinite polymer chains. © 2005 American Institute of Physics. [DOI: 10.1063/1.2102899]

I. INTRODUCTION

In several studies physical properties of infinite polymer chains have been obtained by calculating the desired property for a series of oligomers of increasing length and subsequently extrapolating these results to the infinite polymer limit. In the case of polyacetylene Kirtman *et al.* found that the equilibrium geometry, energy per monomer unit (C_2H_2), and isomerization energies had converged at a chain length of three or four monomer units.¹ Other properties such as the ionization potential, band gaps, and band widths of the infinite chain were shown to converge less rapidly, but it was demonstrated that one could obtain them by extrapolating the results of calculations on small chains up to a length of four units. However, the convergence of the static longitudinal linear polarizability per unit cell, $\alpha_{zz}(N)/N$, of polymers with increasing chain length has been found to be very slow in general (see, for example, Refs. 2–7). Here $\alpha_{zz}(N)$ is the longitudinal linear polarizability of a polymer chain containing N monomer units where its axis is parallel to the applied field, which is chosen to be in the z direction. A consequence of this slow convergence with increasing chain length is that it is very difficult to obtain an accurate value for the polarizability per unit cell of the infinite polymer chain by extrapolation of the results from calculations on oligomer chains because, in general, the correct form of the extrapolation function is not known.

The aim of this work is to provide a relation between the polarizability per unit cell of oligomers and their corresponding infinite polymer chains based on a physical model. The reason we need a physical model is twofold. First, we need it to relate the susceptibility of our infinite polymer chain calculated using periodic boundary conditions to the polarizability per unit cell, which is defined only for finite systems, in the limit to infinite length of the chain. Second, we need a model to establish in which way the polarizability per unit cell converges to the infinite polymer limit. Most extrapolation methods currently available lack a physical basis, rendering them inadequate to make the connection between the polarizability per unit cell of oligomers with that of the infinite polymer chain. They are mainly concerned with achieving high stability and efficiency. These methods assume a linear behavior of the polarizability as a function of the number of units yielding a finite value for the polarizability per unit for the infinite polymer chain. However, the way in which this limit is approached is highly sensitive to the chosen fit form. Moreover, the exact behavior is unknown. For this reason some studies have been performed that do have a physical basis and thus are able to provide this information. Such studies are those by Rojo and Mahan⁸ and Tretiak *et al.*⁹ They both studied the dependence of the polarizability on the chain length using tight-binding model Hamiltonians, being respectively a Hubbard and a Pariser-Parr-Pople Hamiltonian. Recently, Kudin *et al.* studied a model of a one-dimensional stack of equally spaced and identical localized polarizable charge distributions that are considered pointlike

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with respect to the distance between nearest neighbors.⁷ Their analysis led to the conclusion that the static longitudinal linear polarizability per unit cell, $\alpha_{zz}(N)/N$, has the form of a power series, at least to second order, in $1/N$.

In this work we present a physical model that has at its basis a continuous charge distribution in contrast to the work of Kudin *et al.*,⁷ namely, a dielectric needle. Moreover, by using this model we will establish a connection between the polarizability per unit cell of oligomers and that of the infinite polymer chain, something that could not be achieved in the discrete model. In this model we assume a polymer chain to be well described by a cylindrically shaped nonconducting rod with a radius much smaller than its length. With this model we can explain the linear behavior in the number of unit cells of the polarizability and we can also obtain information on the way the limit of the average polarizability per unit to the infinite polymer chain is approached.

We will show that we arrive at the same conclusion as Kudin *et al.* for the form of $\alpha_{zz}(N)/N$. The aim of this work is, therefore, to obtain an extrapolation model that is physically motivated rather than one that is necessarily more stable or more efficient than other methods.

In a recent paper¹⁰ we evaluated the response of an infinite polyacetylene chain to a macroscopic electric field using time-dependent current-density-functional theory (TDCDFT). The exchange-correlation effects were treated in the adiabatic local-density approximation (ALDA) as well as with the Vignale-Kohn (VK) functional.^{11,12} One of the results was that the static longitudinal linear polarizability per unit cell was greatly decreased upon going from the ALDA to the VK functional. The same result was already observed by van Faassen *et al.* for polyacetylene oligomers as well as for other π -conjugated oligomers.^{5,6} Their VK results for these oligomers greatly improved those obtained within the ALDA, obtaining results at the MP2 level (where available). Also for two σ -conjugated polymers and one nonconjugated polymer they found a reduction of the static polarizability, although not as large as for the π -conjugated systems. In this paper we want to evaluate if our results for infinite polymers are in keeping with results obtained by van Faassen *et al.* for oligomers. This means that we have to find a reliable way to extrapolate the oligomer results for the polarizability per unit cell of oligomer chains to the infinite polymer chain. We define $\bar{\alpha}_{zz}(\infty)$ as the $N \rightarrow \infty$ limit of $\bar{\alpha}_{zz}(N) = \alpha_{zz}(N)/N$, the polarizability divided by the number of monomer units. We will refer to this approach as the average approach because there is also an alternative approach that is used in literature to obtain $\bar{\alpha}_{zz}(\infty)$. In this, so-called difference approach, one evaluates the $N \rightarrow \infty$ limit of $\alpha_{zz}(N) - \alpha_{zz}(N-1)$, the difference in polarizability between two oligomers which differ by one monomer unit. With the currently used fit functions, the difference approach is often used since it has the advantage of faster convergence with increasing chain length. The reason for this is believed to be that the effects of the ends of the polymer chain are removed from consideration in this approach. It is not guaranteed that the difference approach leads to the same asymptotic value for the polarizability per unit cell as the average approach, as is often tacitly assumed. For example, an oscillatory behavior in $\alpha_{zz}(N)/N$ can lead to

a different asymptotic value in the two approaches. Only if end effects decay fast enough for polymer chains of increasing length, such that they leave no contributions in the case of an infinite polymer chain, will the difference approach lead to the same asymptotic value as the average approach. We investigate if this is the case within our physical model, and we will show that within our model both approaches lead to the same asymptotic value, albeit that the asymptotic value is approached very slowly as has also been stressed by Kudin *et al.*⁷ Moreover, we will show that for the model we used the results obtained in the average approach can readily be transformed to those of the difference approach. An advantage of the average approach is that numerical errors are reduced for larger polymer chains because they are divided by N . This is not the case for the difference approach, and these errors may lead to numerical instabilities in the extrapolation procedure. Several extrapolation methods have been proposed so far and a summary is given in the next section.

An altogether different approach to obtain properties of infinite systems is to make use of their translational symmetry and employ periodic boundary conditions. In this way one can directly evaluate the properties of the infinite polymer chain and one avoids the problem of needing to find a good extrapolation method. However, when using periodic boundary conditions the effects of density changes at the end points are artificially removed. As a consequence the dipole moment and the polarizability of such systems become ill defined. Instead, we will show that it is more natural to evaluate the polarization with the dimension of a dipole moment per unit length. This is still a well-defined property for infinite quasi-one-dimensional systems. The polarization is related to the average electric field instead of the external electric field through the electric susceptibility. We will show that it is possible to obtain a relation between the susceptibility of the infinite polymer chain and the polarizability per unit cell of oligomers in the limit of $N \rightarrow \infty$ by adopting a physical model describing the dielectric properties of polymer chains. The physical model we use approximates a polymer chain by a so-called dielectric needle, a nonconducting cylinder with a length much bigger than its radius, having a uniform and isotropic susceptibility. Within this model we can directly obtain the polarizability per unit cell of infinite polymer chains by calculating its susceptibility from a periodic boundary calculation. Furthermore, our dielectric needle model provides us with a means to extrapolate the results for the polarizability per unit cell of oligomer chains to infinite length. The results that we obtain from this extrapolation procedure can then be compared to the results obtained from the periodic boundary calculations. This tells us something about the quality of our model. We have done this comparison for two kinds of polymers: the hydrogen chain and *trans*-polyacetylene. Finally, we will give our results for $\bar{\alpha}_{zz}(\infty)$ of a number of infinite polymer chains.

The outline of this article is as follows. In Sec. II we give a description of the theory we will need. It consists of an overview of extrapolation methods that are already available in the literature, an account of the properties of quasi-one-dimensional dielectric media, and an explanation of the

dielectric needle model that we use to describe polymers. In Sec. III we give the computational details of our calculations on infinite polymer chains using periodic boundary conditions and of our extrapolation method. The results obtained from these calculations are discussed in Sec. IV. Finally, we draw conclusions from our findings in Sec. V.

II. THEORY

A. Extrapolation methods

Several extrapolation procedures of the polarizabilities per unit cell of oligomers have been proposed. The first was by Kirtman, who proposed a least-squares fit of $\alpha_{zz}(N)/N$ to a power series in $1/N$ according to²

$$\alpha_{zz}(N)/N = \sum_{n=0}^N c_n N^{-n}, \quad (1)$$

where c_n are constants. Kirtman had already used this scheme successfully to obtain the extrapolated values for the properties of polyacetylene chains mentioned in the Introduction. Similarly, Hurst *et al.* used the same polynomial expansion to fit $\log \alpha_{zz}(N)/N$.³ In order to emphasize the decaying behavior of the difference between the polarizability per unit cell of the infinite polymer chain and that of oligomer chains of increasing length, Champagne *et al.* proposed a fitting function which has an exponential decreasing behavior according to⁴

$$\alpha_{zz}(N) - \alpha_{zz}(N-1) = a - be^{-cN}, \quad (2)$$

where a, b , and c are constants. The obtained values for $\bar{\alpha}_{zz}(\infty)$ are found to be smaller using this exponential fitting function in comparison with the polynomial fitting function. This is consistent with the faster decay caused by the exponential in Eq. (2). We can solve Eq. (2) for $\alpha_{zz}(N)$, which results in

$$\alpha_{zz}(N) = \alpha_{zz}(k-1) + a(N-k+1) - b \frac{e^{-kc} - e^{-c(N+1)}}{1 - e^{-c}}, \quad (3)$$

where k is the number of unit cells of the smallest oligomer that is taken into account in the fitting procedure. We can rewrite Eq. (3) as

$$\frac{\alpha_{zz}(N)}{N} = a + \frac{d}{N} + \frac{f}{N} e^{-cN}, \quad (4)$$

where d and f are new constants combining the constants appearing in Eq. (3). A different fitting function that could be used is the so-called logistic equation, which was proposed in Ref. 13 for the extrapolation of the first hyperpolarizability. Other fitting procedures that have been proposed deal with Padé approximants or are based on purely mathematical approaches.^{14,15} The problem with these fitting methods is that they are not derived from a physical model for the polymer chains. In this sense these extrapolation functions are arbitrary. As mentioned in the Introduction there are some works in the literature that are based on physical models such as those by Rojo and Mahan,⁸ Tretiak *et al.*,⁹ and recently by Kudin *et al.*⁷ From the analysis in the work by Kudin *et al.* it was shown that $\alpha_{zz}(N)/N$ has the form of a

power series in $1/N$ as given in Eq. (1), at least to second order in $1/N$. This means that they confirm the scheme proposed by Kirtman at least up to second order in $1/N$ and the scheme proposed by Champagne *et al.* up to first order in $1/N$.

B. Infinite quasi-one-dimensional dielectric media

A direct manner to obtain properties of infinite quasi-one-dimensional dielectric media is to make use of their translational symmetry and employ periodic boundary conditions. Other works in which infinite quasi-one-dimensional systems are studied are, for example, Refs. 16 and 17, in which coupled-perturbed Hartree-Fock is used. However, when using periodic boundary conditions the effects of density changes at the end points are artificially removed. Let us now evaluate the consequences this has for the evaluation of the polarizability.

In a finite system the polarizability tensor $\alpha(\mathbf{r}, \tau)$ can be obtained from the relation between the induced electric dipole moment $\Delta\boldsymbol{\mu}(t)$ and the external electric field $\mathbf{E}_{\text{ext}}(\mathbf{r}, t)$ according to

$$\Delta\boldsymbol{\mu}(t) = \int_{t_0}^t \int_V \boldsymbol{\alpha}(\mathbf{r}, t-t') \cdot \mathbf{E}_{\text{ext}}(\mathbf{r}, t') d\mathbf{r} dt', \quad (5)$$

where the space integral is over the volume of the entire system, V . The induced dipole moment is defined by

$$\Delta\boldsymbol{\mu}(t) = - \int_V \mathbf{r} \delta\rho(\mathbf{r}, t) d\mathbf{r}, \quad (6)$$

in which $\delta\rho(\mathbf{r}, t)$ is the induced density. It becomes immediately clear that for an infinite quasi-one-dimensional system described with periodic boundary conditions $\Delta\boldsymbol{\mu}(t)$ becomes ill defined. This means that the polarizability tensor in infinite systems is ill defined as well. However, we can also derive an expression for $\Delta\boldsymbol{\mu}(t)$ in terms of the current density $\delta\mathbf{j}(\mathbf{r}, t)$. Starting from Eq. (6) and using the continuity equation, $-\partial_t \delta\rho(\mathbf{r}, t) = \nabla \cdot \delta\mathbf{j}(\mathbf{r}, t)$, we obtain

$$\begin{aligned} \Delta\boldsymbol{\mu}(t) = & - \int_{t_0}^t \int_V \delta\mathbf{j}(\mathbf{r}, t') d\mathbf{r} dt' \\ & + \int_{t_0}^t \int_S \mathbf{r} \delta\mathbf{j}(\mathbf{r}, t) \cdot \mathbf{n} dS dt', \end{aligned} \quad (7)$$

where S is the surface of the system. Since in finite systems there are no currents flowing across S , the surface integral vanishes.

We are considering an infinite quasi-one-dimensional system, therefore we have the assumption that the induced current density is lattice periodic. We can now define the polarization as an induced dipole moment per unit length $\Delta\bar{\boldsymbol{\mu}}(t)$ according to

$$\Delta\bar{\boldsymbol{\mu}}(t) = - \frac{1}{L} \int_{t_0}^t \int_L \int_S \delta\mathbf{j}(\mathbf{r}_{\perp}, z, t') dS dz dt', \quad (8)$$

where L is the length of a unit cell of a quasi-one-dimensional system with its axis in the z direction, S is the surface that cuts the system parallel to the xy plane, and

$\mathbf{r}_\perp = (x, y)$. In this way effects caused by the end points are implicitly accounted for. For example, when an infinite quasi-one-dimensional system is perturbed by an electric field, there will be a current flowing through the interior with a nonzero average along its axis given by $\mathbf{j}(t) = (1/\Lambda) \int_\Lambda \int_S \mathbf{j}(\mathbf{r}_\perp, z, t) dS dz$, which is the average current over an arbitrary length Λ . This current is directly related through the continuity equation to a density change at the end points of the system. It is therefore not necessary to consider end effects explicitly. So the induced dipole moment per unit length $\Delta\bar{\boldsymbol{\mu}}(t)$ is a well-defined quantity also for infinite quasi-one-dimensional systems.

The induced current, and therefore $\Delta\bar{\boldsymbol{\mu}}(t)$, depends not only on the external electric field but also on the field that is induced inside the one-dimensional dielectric medium caused by this external field. It is therefore more natural to relate $\Delta\bar{\boldsymbol{\mu}}(t)$ to the average electric field. We define the average electric field $\bar{\mathbf{E}}(\mathbf{r}_\perp, t)$ as an average over the length of a unit cell of the external electric field plus the induced electric field:

$$\bar{\mathbf{E}}(\mathbf{r}_\perp, t) = \frac{1}{L} \int_L [\mathbf{E}_{\text{ext}}(\mathbf{r}_\perp, z, t) + \mathbf{E}_{\text{ind}}(\mathbf{r}_\perp, z, t)] dz. \quad (9)$$

We can now define the induced dipole moment per unit length $\Delta\bar{\boldsymbol{\mu}}(t)$ as the response to an average electric field rather than an external field according to

$$\Delta\bar{\boldsymbol{\mu}}(t) = \int_{t_0}^t \int_S \boldsymbol{\chi}(\mathbf{r}_\perp, t - t') \cdot \bar{\mathbf{E}}(\mathbf{r}_\perp, t') dS dt', \quad (10)$$

which defines the electric susceptibility $\boldsymbol{\chi}(\mathbf{r}_\perp, \tau)$ as the constant of proportionality.

In this work we would like to obtain a relation between the polarizability per unit cell and the susceptibility of infinite polymer chains, or in other words to establish the following relation

$$\Delta\bar{\boldsymbol{\mu}}(t) = \lim_{N \rightarrow \infty} \frac{\Delta\boldsymbol{\mu}(N, t)}{NL}, \quad (11)$$

where we made explicit that $\Delta\boldsymbol{\mu}(N, t)$ is the induced dipole moment for the oligomer containing N monomer units. To obtain this relation we adopt a physical model for polymer chains, namely, that of a dielectric needle. The main reason that we adopt this model is that, in contrast to real polymer chains, we can evaluate the polarizability of the dielectric needle in the limit of infinite length in an analytic way. This is the subject of the next section.

C. The dielectric needle

We consider a dielectric needle model. A similar model was considered by Fixman.¹⁸ We define the polarization to first order, $\mathbf{P}(\mathbf{r}, \omega)$, as

$$\mathbf{P}(\mathbf{r}, \omega) = -\frac{i}{\omega} \delta \mathbf{j}(\mathbf{r}, \omega), \quad (12)$$

where the Fourier transform is defined as

$$\mathbf{j}(\mathbf{r}, t) = \int \mathbf{j}(\mathbf{r}, \omega) e^{-i\omega t} d\omega. \quad (13)$$

Similar transforms are used for other quantities. The macroscopic polarization $\mathbf{P}_{\text{mac}}(\mathbf{r}, \omega)$, is defined as the average of $\mathbf{P}(\mathbf{r}, \omega)$ over a volume element according to

$$\mathbf{P}_{\text{mac}}(\mathbf{r}, \omega) = \frac{1}{V_r} \int_{V_r} \mathbf{P}(\mathbf{r}', \omega) d\mathbf{r}' = -\frac{i}{\omega V_r} \int_{V_r} \delta \mathbf{j}(\mathbf{r}', \omega) d\mathbf{r}', \quad (14)$$

where V_r is a volume element surrounding the point \mathbf{r} with a size that is small compared to the wavelength of the perturbing field but large enough to contain a large number of bulk unit cells. In analogy to Eq. (9) we now define a macroscopic electric field $\mathbf{E}_{\text{mac}}(\mathbf{r}, \omega)$ as the spatial average over V_r of the external electric field plus the induced electric field,

$$\mathbf{E}_{\text{mac}}(\mathbf{r}, \omega) = \frac{1}{V_r} \int_{V_r} [\mathbf{E}_{\text{ext}}(\mathbf{r}', \omega) + \mathbf{E}_{\text{ind}}(\mathbf{r}', \omega)] d\mathbf{r}'. \quad (15)$$

Note that Eq. (15) is only well defined in a three-dimensional dielectricum, as V_r is ill defined in one- and two-dimensional systems, whereas Eq. (9) is well defined in (quasi-)one-dimensional dielectric media. We now consider a cylinder having radius \mathcal{R} and length \mathcal{L} . We assume that this rodlike system is not conducting, that it has a uniform and isotropic electric susceptibility $\chi_e(\omega)$. We can now write the macroscopic polarization $\mathbf{P}_{\text{mac}}(\mathbf{r}, \omega)$, as

$$\mathbf{P}_{\text{mac}}(\mathbf{r}, \omega) = \chi_e(\omega) \cdot [\mathbf{E}_{\text{ext}}(\mathbf{r}, \omega) + \mathbf{E}_{\text{ind}}(\mathbf{r}, \omega)], \quad (16)$$

with $\chi_e(\omega)$ as a constant of proportionality. Of course, higher-order susceptibilities could be included in Eq. (16) to go beyond the linear-response regime we discuss here. The induced electric field can be obtained from

$$\mathbf{E}_{\text{ind}}(\mathbf{r}, \omega) = -\nabla \int_{\text{Cylinder}} \frac{\mathbf{P}_{\text{mac}}(\mathbf{r}', \omega) \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (17)$$

For reasons of simplicity we will assume that the rod is indeed needlelike, i.e., the ratio \mathcal{R}/\mathcal{L} is small, and that it is placed in a uniform external field $\mathbf{E}_{\text{ext}}(\omega)$ oriented parallel to the axis of the cylinder. In this case we can safely assume that the electric field is not dependent on the distance to the cylinder axis and that both the polarization and the induced field are parallel to this axis. We get for the induced field at the axis in cylindrical coordinates,

$$E_{\text{ind}}(z, \omega) = -\frac{\partial}{\partial z} \int_{-\mathcal{L}/2}^{\mathcal{L}/2} \int_0^{\mathcal{R}} \frac{P_{\text{mac}}(z', \omega)(z - z')}{[(z - z')^2 + (r')^2]^{3/2}} 2\pi r' dr' dz'. \quad (18)$$

Performing the integration and the differentiation we obtain

$$E_{\text{ind}}(z, \omega) = -4\pi P_{\text{mac}}(z, \omega) + 2\pi \int_{-L/2}^{L/2} P_{\text{mac}}(z', \omega) \frac{\mathcal{R}^2}{[(z-z')^2 + \mathcal{R}^2]^{3/2}} dz' \quad (19)$$

Inserting Eq. (16) and introducing the dimensionless coordinates $\zeta = z/\mathcal{L}$ and $\xi = \mathcal{R}/\mathcal{L}$ result in

$$p(\zeta, \omega) = \beta(\omega) \int_{-1/2}^{1/2} p(\zeta', \omega) K(\zeta - \zeta') d\zeta' + \gamma(\omega), \quad (20)$$

in which $p(\zeta, \omega) = P_{\text{mac}}(\mathcal{L}\zeta, \omega)$ and where we defined

$$K(\zeta) = \frac{\xi^2}{(\zeta^2 + \xi^2)^{3/2}}, \quad (21)$$

$$\beta(\omega) = \frac{2\pi\chi_e(\omega)}{1 + 4\pi\chi_e(\omega)}, \quad (22)$$

$$\gamma(\omega) = \frac{\chi_e(\omega)E_{\text{ext}}(\omega)}{1 + 4\pi\chi_e(\omega)}. \quad (23)$$

The expression in Eq. (20) is a standard Fredholm equation of the second kind. Unless $\beta(\omega)$ happens to be a characteristic value of the integral kernel, this equation has a unique solution. If $p(\zeta, \omega)$ can be expanded in a Taylor series for $|\zeta| < 1/2$, the integral in Eq. (20) is equal to $2p(\zeta, \omega)$ in the limit $\xi \rightarrow 0$ under certain assumptions. We show this in Appendix A. One then immediately obtains the following relation for a dielectric rod of infinite length, i.e., in the limit $\xi \rightarrow 0$:

$$\lim_{\xi \rightarrow 0} p(\zeta, \omega) = \chi_e(\omega)E_{\text{ext}}(\omega). \quad (24)$$

So in the case of the infinite dielectric needle, the polarization is uniform. Moreover, we have shown that in the case of an infinite dielectric rod the induced field vanishes and the macroscopic field is equal to the external field for any (finite) radius. This means that the effects caused by the charge buildup at the ends of a dielectric rod decay when the length of the rod is increased. As a result end effects do not lead to macroscopic screening in the infinite dielectric needle. For large $\chi_e(\omega)$ the factor $\beta(\omega)$ in the integral equation of Eq. (20) approaches the characteristic value and the Fredholm equation becomes singular. Therefore we can expect a singular behavior for large $\chi_e(\omega)$ in combination with small ξ .

We now assume that the result we obtained within the model for the infinite dielectric needle, namely, that the average induced field vanishes, is also valid in the case of real polymer chains of infinite length. We then obtain from Eqs. (9) and (10) for a polymer chain of infinite length

$$\Delta\bar{\mu}(\omega) = E_{\text{ext}}(\omega) \int_S \chi_{zz}(\mathbf{r}_\perp, \omega) dS. \quad (25)$$

This enables us to define $\bar{\alpha}_\infty(\omega)$ as the polarizability per unit for a polymer chain of infinite length as

$$\bar{\alpha}_\infty(\omega) = L \frac{\Delta\bar{\mu}(\omega)}{E_{\text{ext}}(\omega)} = L \int_S \chi_{zz}(\mathbf{r}_\perp, \omega) dS. \quad (26)$$

In the case of a dielectric needle of infinite length this equation becomes

$$\bar{\alpha}_\infty(\omega) = \pi\mathcal{R}^2 L \chi_e(\omega). \quad (27)$$

We now want to compare this result for the truly infinite dielectric needle with that of a finite dielectric needle in the limit to infinite length. For a dielectric needle of finite length we obtain the following relation from Eqs. (7) and (14);

$$\Delta\mu(\omega) = \pi\mathcal{R}^2 \mathcal{L} \int_{-1/2}^{1/2} p(\zeta, \omega) d\zeta. \quad (28)$$

Inserting Eq. (5) and dividing both sides by N we obtain ($\mathcal{L} = LN$),

$$\frac{\alpha_{zz}(N, \omega)}{N} = \frac{\pi\mathcal{R}^2 L}{E_{\text{ext}}(\omega)} \int_{-1/2}^{1/2} p(\zeta, \omega) d\zeta, \quad (29)$$

where we defined

$$\alpha_{zz}(N, \omega) = \int_{NV} \alpha(\mathbf{r}, \omega) d\mathbf{r}, \quad (30)$$

in which V is the volume of a unit cell. We can evaluate analytically the polarizability per unit of a dielectric needle of infinite length by taking the limit $N \rightarrow \infty$ in Eq. (29). We obtain

$$\bar{\alpha}_{zz}(\infty, \omega) \equiv \lim_{N \rightarrow \infty} \frac{\alpha_{zz}(N, \omega)}{N} = \pi\mathcal{R}^2 L \chi_e(\omega), \quad (31)$$

where we used the result of Eq. (24). We see that in the case of a dielectric needle we can obtain $\bar{\alpha}_{zz}(\infty, \omega)$ directly from the susceptibility $\chi_e(\omega)$. Comparing this result to Eq. (27) we have

$$\bar{\alpha}_\infty(\omega) = \bar{\alpha}_{zz}(\infty, \omega). \quad (32)$$

In the remainder of the paper we show that this result also holds for real polymer chains, which means that we can obtain $\bar{\alpha}_{zz}(\infty, \omega)$ for real polymers from

$$\bar{\alpha}_{zz}(\infty, \omega) \equiv \lim_{N \rightarrow \infty} \frac{\alpha_{zz}(N, \omega)}{N} = L \int_S \chi_{zz}(\mathbf{r}_\perp, \omega) dS. \quad (33)$$

This is our main result. The integral in Eq. (33) can be evaluated by applying periodic boundary conditions so that there is no need for an extrapolation procedure to obtain $\bar{\alpha}_{zz}(\infty, \omega)$. The validity to apply the results obtained with the dielectric needle model to real polymer chains can be checked explicitly. This is done by fitting the polarizabilities per unit cell of finite oligomer chains to the dielectric needle model using Eq. (29), in which the only fitting parameters are the radius \mathcal{R} and the susceptibility $\chi_e(\omega)$. The best-fit values for \mathcal{R} and $\chi_e(\omega)$ can then be used to obtain $\bar{\alpha}_{zz}(\infty, \omega)$ from Eq. (31). Comparing this result for the extrapolated value at infinite length to that obtained with a periodic boundary calculation will give a direct estimate of the quality of the dielectric needle model for real systems.

The above procedure can be extended to the non-linear-response regime. As mentioned above this means one has to include higher-order susceptibilities in the expression for the macroscopic polarization, Eq. (16). One is then able to study the dependence of hyperpolarizabilities on the chain length. It would be interesting to know, for example, if the induced field would still vanish in the limit of the infinite dielectric needle when these hyperpolarizabilities are considered and how these hyperpolarizabilities approach the infinite limit. To the best of our knowledge, the only work that has gone beyond the linear-response regime using a physical model is that by Rojo and Mahan.⁸ They used a Hubbard model to study the dependence of the second hyperpolarizability on the chain length.

D. Approximate solution of the Fredholm equation

In this section we want to discuss an iterative solution of Eq. (20) to give some insight into our model. We follow the same line of reasoning as Gusmão¹⁹ for his treatment of Love's integral equation,^{20–22} which is very similar to our integral equation, the difference being that the power of the denominator in the kernel is 1 instead of 3/2. We are interested in the limit that ξ is very small. In that case the kernel is sharply peaked. The main contribution to the integral over the kernel therefore comes from the region $\zeta \approx \zeta'$ and as a first approximation we may therefore replace ζ' by ζ in the argument of p under the integral sign. This yields the following equation for the approximate solution $p_0(\zeta)$:

$$p_0(\zeta) = \beta p_0(\zeta) \int_{-1/2}^{1/2} K(\zeta - \zeta') d\zeta' + \gamma, \quad (34)$$

where we suppressed the ω dependence for notational convenience and will continue to do so in the following. The solution $p_0(\zeta)$ is given by

$$p_0(\zeta) = \gamma \left[1 - \beta \left(\frac{(\zeta + 1/2)}{\sqrt{(\zeta + 1/2)^2 + \xi^2}} - \frac{(\zeta - 1/2)}{\sqrt{(\zeta - 1/2)^2 + \xi^2}} \right) \right]^{-1}. \quad (35)$$

We see that for $\xi \rightarrow 0$ and $|\zeta| < 1/2$ we have $p_0 = \chi E_{\text{ext}}$. Moreover, at the end points we have

$$p_0(\pm 1/2) = \frac{\gamma}{1 - \beta(1/\sqrt{1 + \xi^2})}. \quad (36)$$

To give an impression what $p_0(\zeta)/E_{\text{ext}}$ looks like we plot its solution for $\xi=0.01$ and $\chi_e=1$ in Fig. 1 together with the exact solution, $p(\zeta)/E_{\text{ext}}$, from Eq. (20). We see that in the middle of the dielectric needle $p(\zeta)/E_{\text{ext}}$ and $p_0(\zeta)/E_{\text{ext}}$ are close to uniform and rapidly decrease close to the end points. This behavior is enhanced for smaller values of ξ and smaller values of χ_e . The region in which $p_0(\zeta)/E_{\text{ext}}$ is close to uniform is somewhat larger than that for the exact solution, and $p_0(\zeta)/E_{\text{ext}}$ falls off faster than the exact solution near the end points. Furthermore, we observe that in the center of the dielectric needle $p(\zeta)/E_{\text{ext}}$ as well as $p_0(\zeta)/E_{\text{ext}}$ are equal to $\chi_e (=1)$.

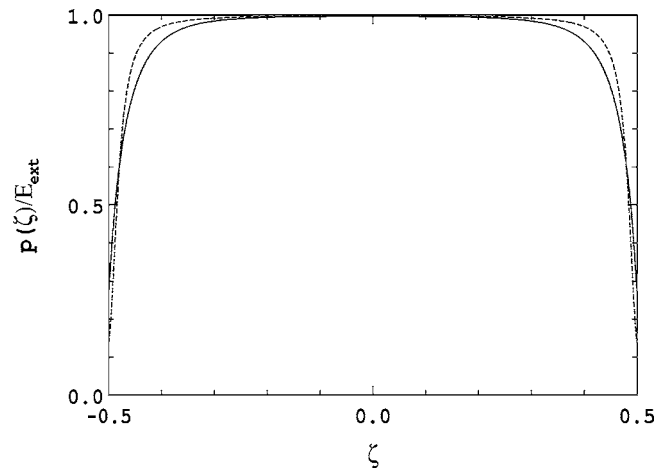


FIG. 1. The static polarization divided by the external field along a dielectric needle for $\chi_e=1$ and $\xi=0.01$. Continuous curve: exact solution $p(\zeta)$; dashed curve: approximate solution $p_0(\zeta)$.

Let us now obtain the average polarization of $p_0(\zeta)$ over the length of the dielectric needle. We define the average polarization of $p(\zeta)$ by

$$\bar{p} = \int_{-1/2}^{1/2} p(\zeta) d\zeta. \quad (37)$$

We have a similar expression for \bar{p}_0 . As is shown in Appendix B we obtain for \bar{p}_0 to first order in ξ ,

$$\bar{p}_0^{[1]} = \chi_e E_{\text{ext}} + 2\gamma\xi h(\beta, 0), \quad (38)$$

where $h(\beta, 0)$ is a constant given in Eq. (B10). Similarly we can obtain \bar{p}_0 up to higher orders of ξ . To order ξ^4 we obtain the following form for \bar{p}_0 :

$$\bar{p}_0 = \chi_e E_{\text{ext}} + A\xi + B\xi^2 + C\xi^3 + D\xi^4 + E\xi^4 \ln \xi + O(\xi^5). \quad (39)$$

So we find that \bar{p}_0 to third order in ξ behaves like a polynomial, but the logarithmic term shows that the correct form of \bar{p}_0 is more complicated. Similar nonanalytic terms involving logarithms that we find for \bar{p}_0 in Eq. (39) were obtained by Gusmão¹⁹ in his treatment of Love's integral equation. In Fig. 2 we plot $\bar{p}_0^{[1]}/E_{\text{ext}}$ together with \bar{p}_0/E_{ext} and the exact solution \bar{p}/E_{ext} . We observe that \bar{p}_0/E_{ext} is a reasonable approximation for \bar{p}/E_{ext} for small ξ and becomes better for larger ξ . Furthermore, we see that $\bar{p}_0^{[1]}/E_{\text{ext}}$ is still a reasonable approximation for the exact solution \bar{p}/E_{ext} for $\xi < 0.1$. We also see that in the limit $\xi \rightarrow 0$ the exact solution and the approximate solution \bar{p}_0/E_{ext} go to $\chi_e (=1)$, which indicates that the assumptions made in deriving Eq. (24) were justified and that indeed the macroscopic part of the induced electric field vanishes in the limit $\xi \rightarrow 0$. We note that for the exact and the approximate solution this limit is approached linearly (albeit with different slopes). We thereby confirm the $1/N$ convergence of $\alpha_{zz}(N)/N$ to its asymptotic value found by Kudin *et al.*⁷ The results obtained for $\alpha_{zz}(N, \omega)/N$ can easily be transformed to obtain the corresponding results for $\alpha_{zz}(N, \omega) - \alpha_{zz}(N-1, \omega)$ by applying a transformation similar to the inverse of the one we performed on Eq. (2). This transformation shows that within our model the difference

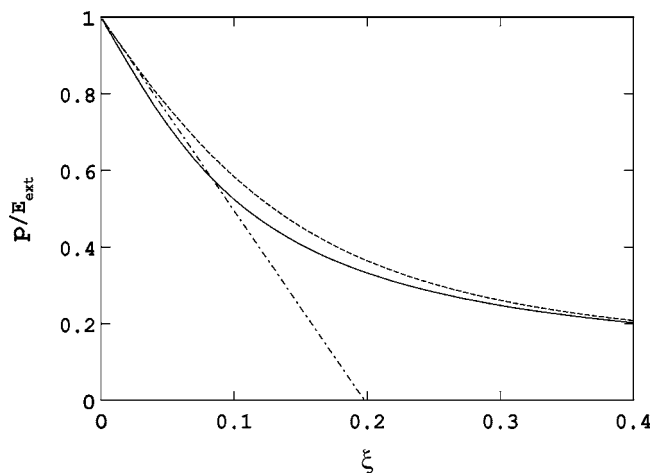


FIG. 2. The average static polarization divided by the external field of a dielectric needle against ξ , the ratio of the radius and the length of the dielectric needle, for $\chi_e=1$. Continuous curve: exact solution \bar{p} ; dashed curve: approximate solution \bar{p}_0 ; dot-dashed curve: $\bar{p}_0^{[1]}$.

approach converges to the same asymptotic value as the average approach. However, we see from the approximate solution in Eq. (39) that $\alpha_{zz}(N, \omega) - \alpha_{zz}(N-1, \omega)$ approaches its asymptotic value as $1/N^2$ instead of $1/N$. We also see from Eq. (39) that successive elimination of higher-order terms in $1/N$, for example, using the Romberg interpolation, will eventually fail due to the nonanalytic behavior of \bar{p}_0 in $\xi=0$.

III. COMPUTATIONAL DETAILS

A. Periodic boundary calculations

The calculations were done in a modified version of the ADF-BAND program.^{10,23–27} We made use of Slater-type orbitals (STO) in combination with frozen cores and a hybrid valence basis set consisting of the numerical solutions of a free-atom Herman-Skillman program²⁸ that solves the radial Kohn-Sham equations. The spatial resolution of this basis is equivalent to a STO triple-zeta basis set augmented with two polarization functions, which was the basis used in Refs. 5 and 6 for the oligomer calculations. This valence basis set was made orthogonal to the core states. The Herman-Skillman program also provides us with the free-atom effective potential. The Hartree potential was evaluated using an auxiliary basis set of STO functions to fit the deformation density in the ground-state calculation and the induced density in the response calculation. For the evaluation of the \mathbf{k} -space integrals we used a numerical integration scheme with 101 symmetry-unique sample points in the irreducible wedge of the Brillouin zone, which was constructed by adopting a Lehmann-Taut tetrahedron scheme.²⁹ We made use of the Vosko-Wilk-Nusair parametrization³⁰ of the local-density approximation (LDA) exchange-correlation potential, which was also used to construct the ALDA exchange-correlation kernel. In the VK calculations we need the static transverse exchange-correlation kernel, $f_{\text{xcT}}(\rho_0, \omega=0)$. They were obtained from Ref. 31, because these values were also used by van Faassen *et al.*

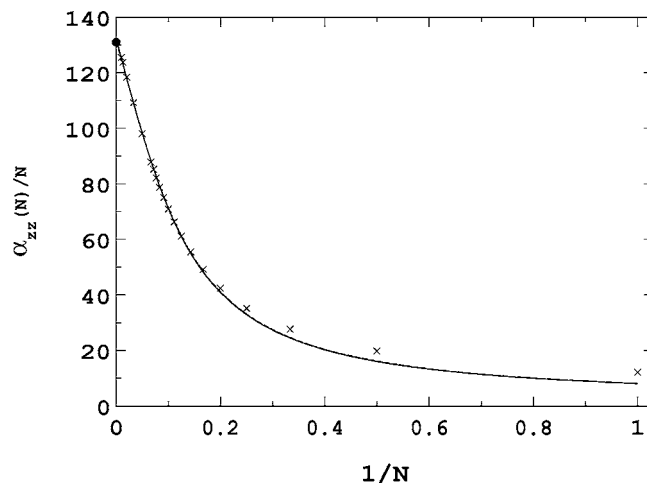


FIG. 3. The polarizability per unit cell $\alpha_{zz}(N)/N$ of the hydrogen chain obtained with TDCDFT using the VK functional. Crosses: oligomer results from Ref. 5; dashed curve: least-squares fit of the oligomer results to our dielectric needle model; continuous curve: least-squares fit of the oligomer results to our dielectric needle model where the results of the smallest five oligomers were discarded; dot: infinite chain result from a periodic boundary calculation.

However, $f_{\text{xcT}}(\rho_0, \omega=0)$ is known only at specific values of the Wigner-Seitz radius r_s ($4\pi r_s^3/3 = 1/\rho_0$). We used a cubic spline interpolation to obtain values of $f_{\text{xcT}}(\rho_0, \omega=0)$ at arbitrary r_s in which the behavior for small r_s was taken to be quadratic, similar to exchange-only behavior. The integral of $\chi_{zz}(\mathbf{r}_\perp, \omega)$ over the surface S in Eq. (33) is solved numerically with the integration scheme in Ref. 25. We performed periodic boundary calculations on the following infinite polymer chains: the hydrogen chain (H), polyacetylene (PA), polyyne (PY), polymethineimine (PMI), polydiacetylene (PDA), polybutatriene (PBT), polythiophene (PT), polyethylene (PE), polysilane (PSi), and polysilene (PSi₂). The geometries of these polymer chains were taken from Refs. 5 and 6. We have checked that the results were converged with respect to all parameters involved in the calculations. To be consistent we used a basis set and a numerical integration scheme in our periodic boundary calculations that were equivalent to those used in the oligomer calculations.

B. Extrapolation

The longitudinal linear polarizabilities per unit cell, $\alpha_{zz}(N)/N$, of several finite hydrogen chains and polyacetylene chains were obtained from Refs. 5 and 32. To fit these results for $\alpha_{zz}(N)/N$ to our dielectric needle model we used the Levenberg-Marquardt method, a standard nonlinear least-squares algorithm. As mentioned above the fit parameters were the radius \mathcal{R} and the electric susceptibility χ_e . The Fredholm equation in Eq. (20) was solved numerically using a Gauss-Legendre quadrature.

IV. RESULTS

In Figs. 3 and 4 we show the static longitudinal polarizabilities per unit cell, $\alpha_{zz}(N)/N$, of several hydrogen chain oligomers and polyacetylene oligomers, respectively, as obtained by van Faassen *et al.*⁵ using TDCDFT with the VK

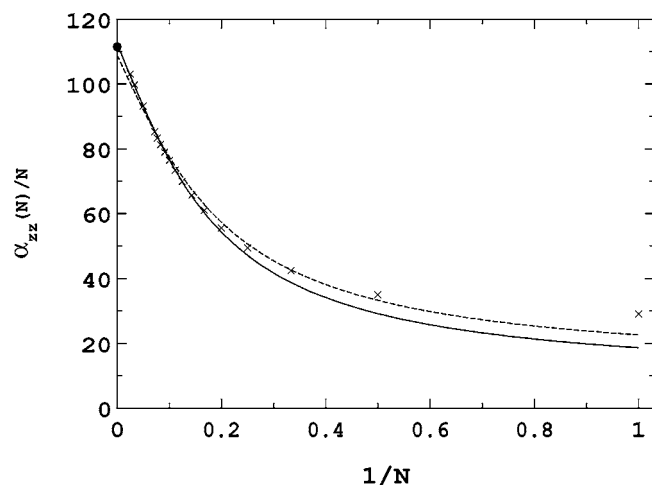


FIG. 4. The polarizability per unit cell $\alpha_{zz}(N)/N$ of polyacetylene obtained with TDCDFT using the VK functional. Crosses: oligomer results from Ref. 5; dashed curve: least-squares fit of the oligomer results to our dielectric needle model; continuous curve: least-squares fit of the oligomer results to our dielectric needle model where the results of the smallest five oligomers were discarded; dot: infinite chain result from a periodic boundary calculation.

functional together with the fits of these values to our dielectric needle model. We see that in the case of the hydrogen chain the fit in which all oligomer results were taken into account is very close to the oligomer results for $N \geq 6$. For this reason and because the dielectric needle model is probably not such a good approximation for the smallest oligomers, we also did a fit in which all oligomer results were taken into account except those for the five smallest oligomer chains. The result is a fit that lies on top of the first one. In the case of polyacetylene the situation is somewhat different. Here it does make a difference whether or not we discard the results of the five smallest oligomers in our fitting scheme. If we do so the fit is much improved for the longer oligomer chains. The fit is then again very close to the oligomer results (for $N \geq 6$). There are two reasons for the fact that in the case of polyacetylene the two fits are different, while in the case of the hydrogen chain they are on top of each other. First, in the case of polyacetylene we have a smaller number of results for the longer oligomers than we have for the hydrogen chain, meaning that the small oligomers have a relatively larger weight in the fit. Second, the ratio of the length and width of a polyacetylene monomer, is smaller than that of a hydrogen chain monomer, which is mainly caused by the hydrogen atoms that are bound almost perpendicular to the direction of the polyacetylene chain. We also applied our fitting procedure to the oligomer results of van Faassen *et al.*⁵ using TDCDFT within the ALDA. The results are shown in Figs. 5 and 6. Here we only show the results for the fits in which the five smallest oligomers have been discarded. Again, the fit is in very good agreement with the oligomer results.

From the fitting procedure of the oligomer results to our dielectric needle model we obtain the best-fit values of our fit parameters, the radius and the electric susceptibility. With these best-fit values we obtain directly $\bar{\alpha}_{zz}(\infty)$ for the infinite polymer chains from Eq. (31). The results are given in Table

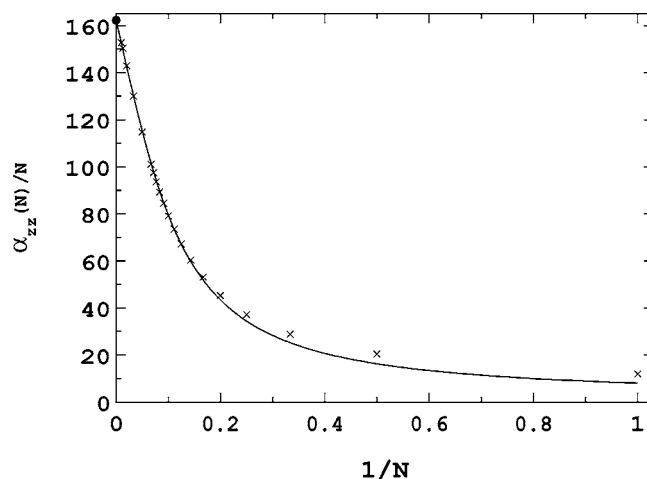


FIG. 5. The polarizability per unit cell $\alpha_{zz}(N)/N$ of the hydrogen chain obtained with TDCDFT using the ALDA. Crosses: oligomer results from Ref. 5; dashed curve: least-squares fit of the oligomer results to our dielectric needle model where the results of the smallest five oligomers were discarded; dot: infinite chain result from a periodic boundary calculation.

I. We see that the results obtained with both methods are nearly the same, the difference being below 1% with the exception of the infinite polyacetylene chain calculated within the ALDA. There we see a difference of about 5%. Along with these results we also listed the results for $\bar{\alpha}_{zz}(\infty)$ in Table I those we obtained using the extrapolation methods of Kirtman and Champagne *et al.* as given in Eqs. (1) and (2), respectively. For the extrapolation method of Kirtman we fitted $\alpha_{zz}(N)/N$ to a third-order polynomial in $1/N$. Instead of fitting $\alpha_{zz}(N)/N$, Champagne *et al.* fitted $\alpha_{zz}(N) - \alpha_{zz}(N-1)$ to an exponential function. However, we do not always have the polarizabilities of polymer chains differing in one monomer unit available. Therefore we fit to Eq. (4), which is the same as fitting to Eq. (2) as was shown above. From Table I we see that, although the results obtained with the extrapolation according to our dielectric needle model lie closest to the results obtained from periodic boundary calcu-

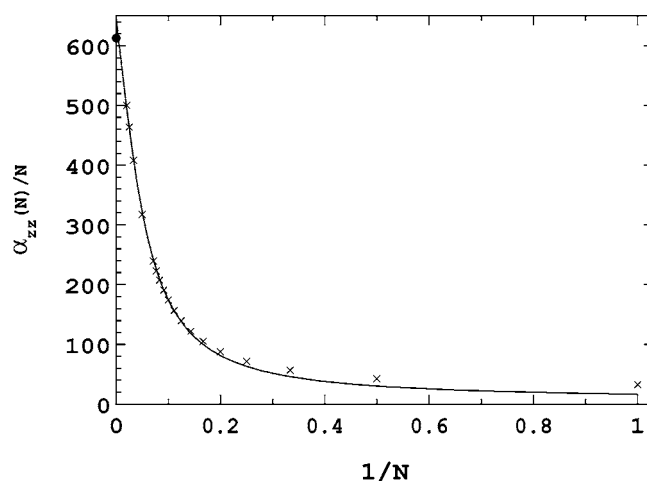


FIG. 6. The polarizability per unit cell $\alpha_{zz}(N)/N$ of polyacetylene obtained with TDCDFT using the ALDA. Crosses: oligomer results from Ref. 5; dashed curve: least-squares fit of the oligomer results to our dielectric needle model where the results of the smallest five oligomers were discarded; dot: infinite chain result from a periodic boundary calculation.

TABLE I. The polarizabilities per unit cell of the infinite polymer chain, $\bar{\alpha}_{zz}(\infty)$, obtained from a calculation using periodic boundary conditions (PBC) and from a fit of the oligomer results to our dielectric needle model, to a polynomial as proposed in Ref. 2, and to an exponential function as proposed in Ref. 4. The results are for the infinite hydrogen chain (H) and the infinite polyacetylene chain (PA) both calculated using TDCDFT within the ALDA as well as with the VK functional.

Polymer (functional)	$\bar{\alpha}_{zz}(\infty)$			
	PBC	Dielectric needle	Polynomial	Exponential
H(VK)	131.01	132.16	133.45	132.40
PA(VK)	111.48	112.44	114.94	113.24
H(ALDA)	162.28	162.26	164.42	162.60
PA(ALDA)	612.78	646.21	668.53	656.77

lations, the differences between the three methods are small. This is not surprising if we compare the extrapolation formulas of Kirtman and Champagne *et al.* in Eqs. (1) and (4), respectively, to our approximate solution $\bar{p}_0(\omega)$ given in Eq. (39). We see that up to third order in $1/N$ we have the same form as Kirtman and up to first order in $1/N$ we have almost the same form as Champagne *et al.* since the exponential in Eq. (4) goes to zero fastly for large N , assuming the constant c is positive. As expected the results obtained with the extrapolation formula of Champagne *et al.* lie lower than those obtained with Kirtman's formula. In Table II we show our best-fit values for the radius \mathcal{R} and the electric susceptibility χ_e . We do not give the radius as such but the ratio $\xi_u = \mathcal{R}/L$ of the radius and the length of a unit cell because it shows in a better way that the best-fit values for the radius are realistic. Now that we have shown that the polarizabilities per unit cell of infinite polymer chains, $\bar{\alpha}_{zz}(\infty)$, from periodic boundary calculations are in keeping with the extrapolated values of $\alpha_{zz}(N)/N$ obtained by van Faassen *et al.*, we present the $\bar{\alpha}_{zz}(\infty)$ for several kinds of polymers obtained from our periodic boundary calculations in Table III. We use TDCDFT within the ALDA as well as with the VK functional. We see that the VK values are greatly reduced for all polymers with respect to the ALDA results. Especially for the π -conjugated systems (PA, PY, PMI, PDA, PBT, PT, and PSi_2), this reduction is substantial.

V. CONCLUSIONS

In this work we presented a physical model for the longitudinal polarizabilities of polymer chains that describes

TABLE II. The ratios, $\xi_u = \mathcal{R}/L$, of the radius and the length of a unit cell and the electric susceptibility χ_e of the hydrogen chain (H) and polyacetylene (PA) obtained from a fit of the oligomer results to our dielectric needle model. The results are calculated using TDCDFT within the ALDA as well as with the VK functional.

Polymer (functional)	$\xi_u = \mathcal{R}/L$	χ_e
H(VK)	0.304	4.98
PA(VK)	0.623	0.907
H(ALDA)	0.300	6.29
PA(ALDA)	0.501	8.06

TABLE III. Polarizabilities per unit cell for various polymer chains of infinite length, $\bar{\alpha}_{zz}(\infty)$, obtained from TDCDFT calculations using periodic boundary conditions within the ALDA and with the VK functional. H: hydrogen chain, PA: polyacetylene, PY: polyyne, PMI: polymethineimine, PDA: polydiacetylene, PBT: polybutatriene, PT: polythiophene, PE: polyethylene, PSi: polysilane, and PSi_2 : polysilene.

Polymer	Monomer unit	$\bar{\alpha}_{zz}(\infty)$	
		ALDA	VK
H	H_2	162.28	131.01
PA	C_2H_2	612.78	111.48
PY	C_2	315.73	143.28
PMI	CNH	352.91	79.70
PDA	C_4H_2	771.46	194.49
PBT	C_4H_2	6017.24	245.07
PT	$\text{C}_8\text{S}_2\text{H}_4$	1162.06	329.63
PE	C_2H_4	36.28	31.67
PSi	Si_2H_4	209.49	101.62
PSi_2	Si_2H_2	6263.73	390.09

their dielectric properties. We showed that within this model we can relate the polarizability per unit cell $\alpha_{zz}(N, \omega)/N$ of oligomers to that of the their corresponding infinite polymer chains. The physical model we use is that of a dielectric needle in which we assume a polymer chain to be well described by a cylindrically shaped nonconducting rod with a radius much smaller than its length. We showed that within this model the macroscopic contribution of the induced electric field to the macroscopic electric field vanishes in the limit of $N \rightarrow \infty$, i.e., there is no macroscopic screening. This identification leads to a relation between $\alpha_{zz}(N, \omega)/N$ in the limit $N \rightarrow \infty$ and the electric susceptibility of the infinite polymer chain. This means that we can obtain the polarizability per unit cell of the infinite polymer chain, $\bar{\alpha}_{zz}(\infty, \omega)$, directly from a periodic boundary calculation. Moreover, by studying an approximate solution of our model and from the information contained in Fig. 2 we conclude that the leading terms in an expansion of $\alpha_{zz}(N, \omega)/N$ is $\bar{\alpha}_{zz}(\infty, \omega) + a/N$, but that higher-order terms become nonanalytic. This means that end effects, which ultimately vanish in the infinite polymer chain, decrease only slowly with increasing chain length. The dielectric needle also provides us with a procedure to extrapolate the results of $\alpha_{zz}(N, \omega)/N$ of oligomer chains to infinite length. Comparing this result for the extrapolated value at infinite length to that obtained with a periodic boundary calculation gives a direct estimate of the validity of using the dielectric needle model. We have tested our extrapolation method on the static longitudinal polarizabilities per unit cell, $\alpha_{zz}(N, \omega=0)/N$, of oligomers of the hydrogen chain and of polyacetylene that were obtained by van Faassen *et al.*⁵ using time-dependent current-density-functional theory in the adiabatic local-density approximation and with the Vignale-Kohn functional. At the same time we performed calculations using the same theory on truly infinite polymer chains by employing periodic boundary conditions. We showed that by extrapolating the oligomer results according to our dielectric needle model we get good agreement with our results from calculations on infinite polymer chains using periodic boundary conditions. This shows that our dielectric

needle model we get good agreement with our results from calculations on infinite polymer chains using periodic boundary conditions. This shows that our dielectric needle model is a good approximation to describe the dielectric properties of long polymer chains. Furthermore, it shows that our results for the infinite polymer chains of the hydrogen chain and polyacetylene, both from ALDA and VK calculations, are in keeping with the oligomer results of van Faassen *et al.*

ACKNOWLEDGMENT

The authors would like to thank M. van Faassen for providing us with additional data for the polarizabilities per unit cell of several oligomers of the hydrogen chain and polyacetylene.

APPENDIX A: INFINITE LIMIT OF THE DIELECTRIC NEEDLE

We define for $|\zeta| < \frac{1}{2}$,

$$I(\zeta, \xi) = \int_{-1/2}^{1/2} p(\zeta', \xi) \frac{\xi^2}{[(\zeta - \zeta')^2 + \xi^2]^{3/2}} d\zeta'. \quad (\text{A1})$$

We now show that we have the following equality:

$$\lim_{\xi \rightarrow 0} I(\zeta, \xi) = 2p(\zeta, 0), \quad (\text{A2})$$

under the assumption that $p(\zeta', \xi)$ can be expanded in a Taylor series around $\zeta' = \zeta$ for $|\zeta| < 1/2$. It is easy to see that we have

$$I(\zeta, \xi) = \int_{-1/2}^{1/2} p(\zeta', \xi) \frac{\partial^2}{\partial \zeta'^2} \sqrt{(\zeta - \zeta')^2 + \xi^2} d\zeta'. \quad (\text{A3})$$

Inserting the Taylor expansion of $p(\zeta', \xi)$ and assuming that we can integrate term by term, we obtain

$$I(\zeta) = \sum_{n=0}^{\infty} I_n(\zeta, \xi), \quad (\text{A4})$$

where

$$I_n(\zeta, \xi) = \frac{1}{n!} p^{(n)}(\zeta, \xi) \int_{-1/2}^{1/2} (\zeta' - \zeta)^n \frac{\partial^2}{\partial \zeta'^2} \sqrt{(\zeta - \zeta')^2 + \xi^2} d\zeta', \quad (\text{A5})$$

in which $p^{(n)}(\zeta, \xi)$ is the n th order derivative of $p(\zeta', \xi)$ with respect to ζ' at ζ . Changing variables according to $\zeta' - \zeta = x$ and performing integration by parts twice we have

$$I_n(\zeta, \xi) = \frac{1}{n!} p^{(n)}(\zeta, \xi) \left\{ \left[x^n \frac{\partial}{\partial x} \sqrt{x^2 + \xi^2} - nx^{n-1} \sqrt{x^2 + \xi^2} \right]_{-1/2-\zeta}^{1/2-\zeta} + n(n-1) \int_{-1/2-\zeta}^{1/2-\zeta} x^{n-2} \sqrt{x^2 + \xi^2} dx \right\}. \quad (\text{A6})$$

Note that $1/2 - \zeta \geq 0$ and $-1/2 - \zeta \leq 0$. In the following we assume that we can interchange the limit of $\xi \rightarrow 0$ with the integrals and that the n th order derivatives of $p(\zeta', \xi)$ are

finite in the limit $\xi \rightarrow 0$. For $n=0$ we then have

$$\lim_{\xi \rightarrow 0} I_0(\zeta, \xi) = p^{(0)}(\zeta, 0) \left[\frac{\partial}{\partial x} |x| \right]_{-\xi^{-1/2}}^{\xi^{-1/2}} = 2p(\zeta, 0). \quad (\text{A7})$$

For $n=1$ we have

$$\lim_{\xi \rightarrow 0} I_1(\zeta, \xi) = p^{(1)}(\zeta, 0) \left[x \frac{\partial}{\partial x} |x| - |x| \right]_{-\xi^{-1/2}}^{\xi^{-1/2}} = 0. \quad (\text{A8})$$

For $n \geq 2$ we have

$$\begin{aligned} \lim_{\xi \rightarrow 0} I_n(\zeta, \xi) &= \frac{1}{n!} p^{(n)}(\zeta, 0) \left\{ \left[x^n \frac{\partial}{\partial x} |x| - nx^{n-1} |x| \right]_{-1/2-\zeta}^{1/2-\zeta} \right. \\ &\quad \left. + n(n-1) \left[\int_{-1/2-\zeta}^0 -x^{n-1} dx + \int_0^{1/2-\zeta} x^{n-1} dx \right] \right\} \\ &= \sum_{n=2}^{\infty} \frac{1}{n!} p^{(n)}(\zeta, 0) \{ [-x^n + nx^{n-1} - (n-1)x^n]_{-1/2-\zeta}^0 \\ &\quad + [x^n - nx^n + (n-1)x^n]_0^{1/2-\zeta} \} = 0. \end{aligned} \quad (\text{A9})$$

Combining the results for all n gives Eq. (A2).

APPENDIX B: ASYMPTOTIC EXPANSION OF \bar{p}_0

To obtain \bar{p}_0 from Eq. (35) we have to solve

$$\bar{p}_0 = 2\gamma \int_0^{1/2} d\zeta \left[1 - \beta \left(\frac{(\zeta + 1/2)}{\sqrt{(\zeta + 1/2)^2 + \xi^2}} - \frac{(\zeta - 1/2)}{\sqrt{(\zeta - 1/2)^2 + \xi^2}} \right) \right]^{-1}, \quad (\text{B1})$$

where we used the fact that the integrand is even. We will evaluate this integral in the limit of small ξ . For the first term in the denominator of this expression we can write to first order in ξ

$$\frac{(\zeta + 1/2)}{\sqrt{(\zeta + 1/2)^2 + \xi^2}} = 1 + O(\xi^2). \quad (\text{B2})$$

We thus obtain

$$\bar{p}_0 = 2\gamma \int_0^{1/2} d\zeta \left[1 - \beta \left(1 - \frac{(\zeta - 1/2)}{\sqrt{(\zeta - 1/2)^2 + \xi^2}} \right) \right]^{-1} + O(\xi^2). \quad (\text{B3})$$

We now make the substitution $\xi x = 1/2 - \zeta$. Then $\bar{p}(\zeta)$ attains the form

$$\bar{p}_0 = 2\gamma \xi \int_0^{1/2\xi} dx \left[1 - \beta \left(1 - \frac{x}{\sqrt{x^2 + 1}} \right) \right]^{-1} + O(\xi^2). \quad (\text{B4})$$

The large x behavior of the integrand to first order in $1/x$ is given by

$$\frac{1}{1 - \beta(1 + (x/\sqrt{x^2 + 1}))} = \frac{1}{1 - 2\beta} + O\left(\frac{1}{x^2}\right). \quad (\text{B5})$$

We can therefore add and subtract the limiting values of the integrand for $\bar{p}_0(x)$ and write

$$\bar{p}_0 = 2\gamma\xi \int_0^{1/2} \frac{1}{1 - 2\beta} dx + 2\gamma\xi h(\beta, \xi) + O(\xi^2) \quad (\text{B6})$$

$$= \frac{\gamma}{(1 - 2\beta)} + 2\gamma\xi h(\beta, \xi) + O(\xi^2), \quad (\text{B7})$$

where we defined

$$h(\beta, \xi) = \int_0^{1/2} \left[\frac{1}{1 - \beta(1 + (x/\sqrt{x^2 + 1}))} - \frac{1}{1 - 2\beta} \right] dx. \quad (\text{B8})$$

We can expand $h(\beta, \xi)$ in a Taylor expansion around $\xi=0$ according to

$$h(\beta, \xi) = h(\beta, 0) + h'(\beta, 0)\xi + O(\xi^2), \quad (\text{B9})$$

where the coefficients $h^{(n)}(\beta, 0)$ can be shown to be finite. The coefficient $h(\beta, 0)$ is given by

$$h(\beta, 0) = -\frac{\beta}{1 - 2\beta} - \frac{2\beta^2}{(1 - 2\beta)^{3/2}} \left[\arctan(\sqrt{1 - 2\beta}) + \arctan\left(\frac{\beta}{\sqrt{1 - 2\beta}}\right) \right]. \quad (\text{B10})$$

Inserting the expansion for $h(\beta, \xi)$ given in Eq. (B9) into Eq. (B7) gives Eq. (38).

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